

# Multicompartment Micelles from ABC Triblock Terpolymers

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## INTRODUCTION

The term multicompartment micelles stands for self-assembled aggregates of block copolymers with cores that are further subdivided. A recent review contributes to the progress within this field of research<sup>1</sup>. Those structures are of great interest when it comes to the simulation or understanding of biological systems, where different functionalities in close proximity are necessary to perform distinct biological functions<sup>2</sup>. In a recent study, Hillmyer et al. showed the storage of two different dyes in two segregated compartments of such a multicompartmental structure in various aqueous micellar solutions<sup>3</sup>.

Complex structures in solution can be prepared from ABC triblock terpolymers<sup>4</sup>. In contrast to the huge amount of reports on micellar aggregates from diblock copolymers or the structures of ABC triblock terpolymers in the bulk, the number of contributions on triblock terpolymer micelles in selective solvents is still limited<sup>5-9</sup>. Also the preparation and the control of the stability of such systems are still at their very beginning. Almost all the current approaches are based on the mutual incompatibility of fluorocarbon and hydrocarbon segments and the self-assembly takes place in aqueous media<sup>2, 3, 10, 11</sup>. One very recent example employs a ABCBA pentablock terpolymer of poly(ethylene oxide), poly( $\gamma$ -benzyl-L-glutamate), and poly(perfluoro ether) (PEO-*b*-PBLG-*b*-PFPE-*b*-PBLG-*b*-PEO) in aqueous solution<sup>12</sup>.

In this contribution we present the formation of multicompartment micelles in acetone solution for a linear polybutadiene-*b*-poly(2-vinylpyridine)-*b*-poly(*tert*-butyl methacrylate) triblock terpolymer, B<sub>30</sub>V<sub>14</sub>T<sub>56</sub><sup>141</sup>, where the indices stand for the weight fractions and the superscript for the molecular weight in kg/mol. The formed aggregates were investigated by transmission electron microscopy (TEM) and light scattering (DLS) methods. The micelles are stable with respect to crosslinking of the remaining double bonds of the polybutadiene compartment. Crosslinking was carried out via cold vulcanization with S<sub>2</sub>Cl<sub>2</sub>. After performing the reactions in solution, the micelles again were subjected to TEM and DLS analysis. In contrast to other works within this field, the building blocks employed here are rather simple and consist of standard easy-to-handle monomers.

## EXPERIMENTAL

**Reagents.** *Sec*-butyllithium (Aldrich) was used without further purification. Butadiene (Messer-Griesheim) was passed through columns filled with molecular sieves (4Å) and basic aluminum oxide and stored over dibutylmagnesium. 2-Vinylpyridine (Fluka) was degassed and stirred with CaH<sub>2</sub> over night. Both 2-vinylpyridine and *tert*-butyl methacrylate were condensed on a high vacuum line and stored at liquid nitrogen temperature until use. THF (Fluka) was distilled from CaH<sub>2</sub> and Na/K alloy. 1,1-Diphenylethylene was distilled from *sec*-butyllithium under reduced pressure.

**Sequential Living Anionic Polymerization in THF** The linear BVT triblock terpolymers were synthesized via sequential living anionic polymerization in THF at low temperatures using *sec*-butyllithium as initiator. Under these conditions, polybutadiene has a predominant 1,2-structure. After the polymerization of the P2VP block, 1,1-diphenylethylene was added to end-cap the living anionic chain ends. The number-average molecular weight of the polybutadiene precursor and the molecular weight distributions of the triblock terpolymers were determined by gel permeation chromatography using PB calibration. The polymer exhibits a narrow molecular weight distribution, characterized by a polydispersity index of 1.03. Additionally, <sup>1</sup>H NMR spectra were recorded and the molecular weights of the P2VP and

PBMA blocks were calculated using the terpolymer composition determined by NMR.

**Transmission Electron Microscopy.** TEM images were taken with a Zeiss CEM 902 or 922 OMEGA electron microscope operated at 80 kV or 200 kV, respectively. Both machines are equipped with an in-column energy filter. Samples were prepared through deposition of a drop of micellar solution (concentration always 0.1 mg/ml) onto the TEM grid (Gold, 250 or 400 mesh). Afterwards the remaining solvent was removed with a filter tip.

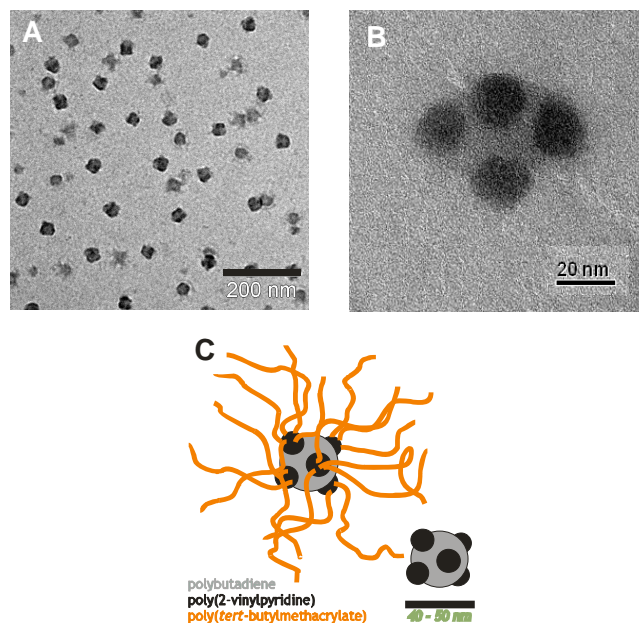
**Gel Permeation Chromatography.** (GPC) measurements were performed on a set of 30 cm SDV-gel columns of 5 mm particle size having a pore size of 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup> and 10<sup>2</sup> Å with RI and UV ( $\lambda$ =254 nm) detection. GPC was measured at an elution rate of 1 ml/min with THF as solvent. Polybutadiene standards were used for calibration.

**<sup>1</sup>H NMR Spectra** were recorded on a Bruker 250 AC spectrometer using either CDCl<sub>3</sub> or THF as solvent and tetramethylsilane (TMS) as internal standard.

**Dynamic Light Scattering (DLS)** measurements were performed on an ALV DLS/SLS-SP 5022F compact goniometer system with an ALV 5000/E correlator and a He-Ne laser. Prior to the light scattering measurements the sample solutions were filtered using Millipore Teflon filters with a pore size of 1  $\mu$ m. CONTIN analysis of the autocorrelation functions was carried out.

## RESULTS

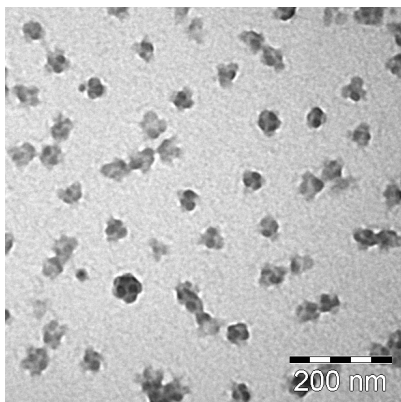
When dissolved in acetone, B<sub>30</sub>V<sub>14</sub>T<sub>56</sub><sup>141</sup> forms micellar aggregates due to the insolubility of the polybutadiene block. Figure 1 shows TEM micrographs of the aggregates. Part B shows one multicompartment micelle at a higher magnification. The visible structures consist of a core with an average diameter of 40-50 nm bearing several black dots with an average diameter of around 15 nm.



**Figure 1.** TEM micrographs of the micellar aggregates of B<sub>30</sub>V<sub>14</sub>T<sub>56</sub><sup>141</sup> from acetone solution (0.1 mg/ml); A overview; B single micellar aggregate; C proposed solution structure.

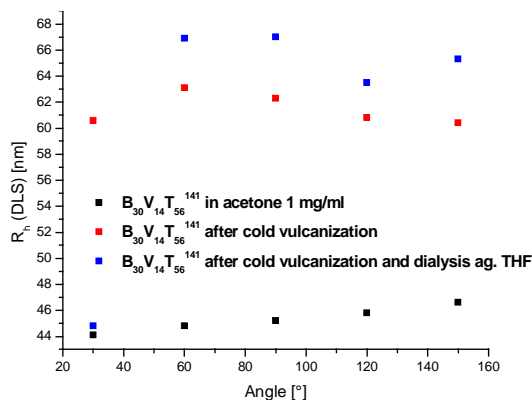
A similar morphology was observed from partially fluorinated ABC triblock terpolymers in aqueous solution<sup>11</sup>. Four to six segregated darker domains are observed for each micellar core. Considering the insolubility of polybutadiene in acetone, the core of the micelles should be formed by that block. From the electron density, poly(2-vinylpyridine) should provide the best contrast and therefore form the dark compartments on the micellar core. Poly(*tert*-butyl methacrylate) is soluble in acetone and should form the corona. Due to the incident

electron beam, the P~~B~~MA block may already been depolymerized<sup>13</sup>. This, in combination with the ABC sequence, leads us to the structure for the multicompartment micelles shown in Figure 1C. Figure 2 shows a TEM micrograph of the same micellar aggregates after crosslinking of the PB block via 'cold vulcanization' with S<sub>2</sub>Cl<sub>2</sub> in acetone solution.



**Figure 2.** TEM micrograph of the micellar aggregates of B<sub>30</sub>V<sub>14</sub>T<sub>56</sub><sup>141</sup> from acetone solution (0.1 mg/ml) after crosslinking with S<sub>2</sub>Cl<sub>2</sub> and subsequent dialysis against acetone.

The B<sub>30</sub>V<sub>14</sub>T<sub>56</sub><sup>141</sup> triblock terpolymers micelles show a very narrow size distribution in acetone solution ( $R_h = 46.4 \pm 1.4$  nm for the uncrosslinked particles,  $61.5 \pm 8.1$  for the crosslinked aggregates at a scattering angle of 90°). To prove the crosslinking of the polybutadiene core, the micelles were dialyzed against THF, which is a non-selective solvent. Again micelles were detected, indicating a successful crosslinking procedure.



**Figure 3:** Hydrodynamic radii (DLS) of the micellar aggregates of B<sub>30</sub>V<sub>14</sub>T<sub>56</sub><sup>141</sup> in acetone solution as a function of the scattering angle.

### CONCLUSION

Multicompartment micelles from linear ABC triblock terpolymers, poly(butadiene)-*b*-poly(2-vinylpyridine)-*b*-poly(*tert*-butylmethacrylate), can be easily prepared by dissolving the polymers in acetone, as shown by TEM measurements. The uniformity of the formed aggregates was proven by dynamic light scattering experiments. Crosslinking of the PB block leads to an increased stability. These objects will now be the subject of further experiments to determine the relationship between the polymer composition and the micellar structure.

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### REFERENCES

- Lutz, J.-F.; Laschewsky, A., *Macromol. Chem. Phys.* **2005**, 206, 813-817.
- Li, Z.; Hillmyer, M. A.; Lodge, T. P., *Macromolecules* **2006**, 39, 765-771.
- Lodge, T.; Rasdal, A.; Li, Z.; Hillmyer, M. A., *J. Am Chem Soc.* **2005**, 127, 17608-17609.
- Underhill, R. S.; Liu, G., *Chem. Mater.* **2000**, 12, 2082-2091.
- Patrickios, C. S.; Forder, C.; Armes, S. P.; Billingham, N. C., *J. Polym. Sci. A: Polym. Chem.* **1997**, 35, 1181.
- Kriz, J.; Massar, B.; Plestil, J.; Tuzar, Z.; Pospisil, H.; Doskocilova, D., *Macromolecules* **1998**, 31, 41.
- Chen, W. Y.; Alexandridis, P.; Su, C. K.; Patrickios, C. S.; Hertler, W. R.; Hatton, T. A., *Macromolecules* **1995**, 28, 8604.
- Yu, G. E.; Eisenberg, A., *Macromolecules* **1998**, 31, (16), 5546-5549.
- Stewart, S.; Liu, G., *Chem. Mater.* **1999**, 11, 1048.
- Stähler, K.; Selb, J.; Candau, F., *Materials Science & Engineering C* **1999**, 10, 171-178.
- Kubowicz, S.; Baussard, J.-F.; Lutz, J.-F.; Thünemann, A.; Berlepsch, H. v.; Laschewsky, A., *Angew. Chem. int. Ed.* **2005**, 44, 5262-5265.
- Thünemann, A.; Kubowicz, S.; Berlepsch, H. v.; Möhwald, H., *Langmuir* **2006**, 22, 2506-2510.
- Ludwigs, S. Complex Nanostructures in triblock terpolymer thin films. Diss., Dissertation, Bayreuth, 2004.